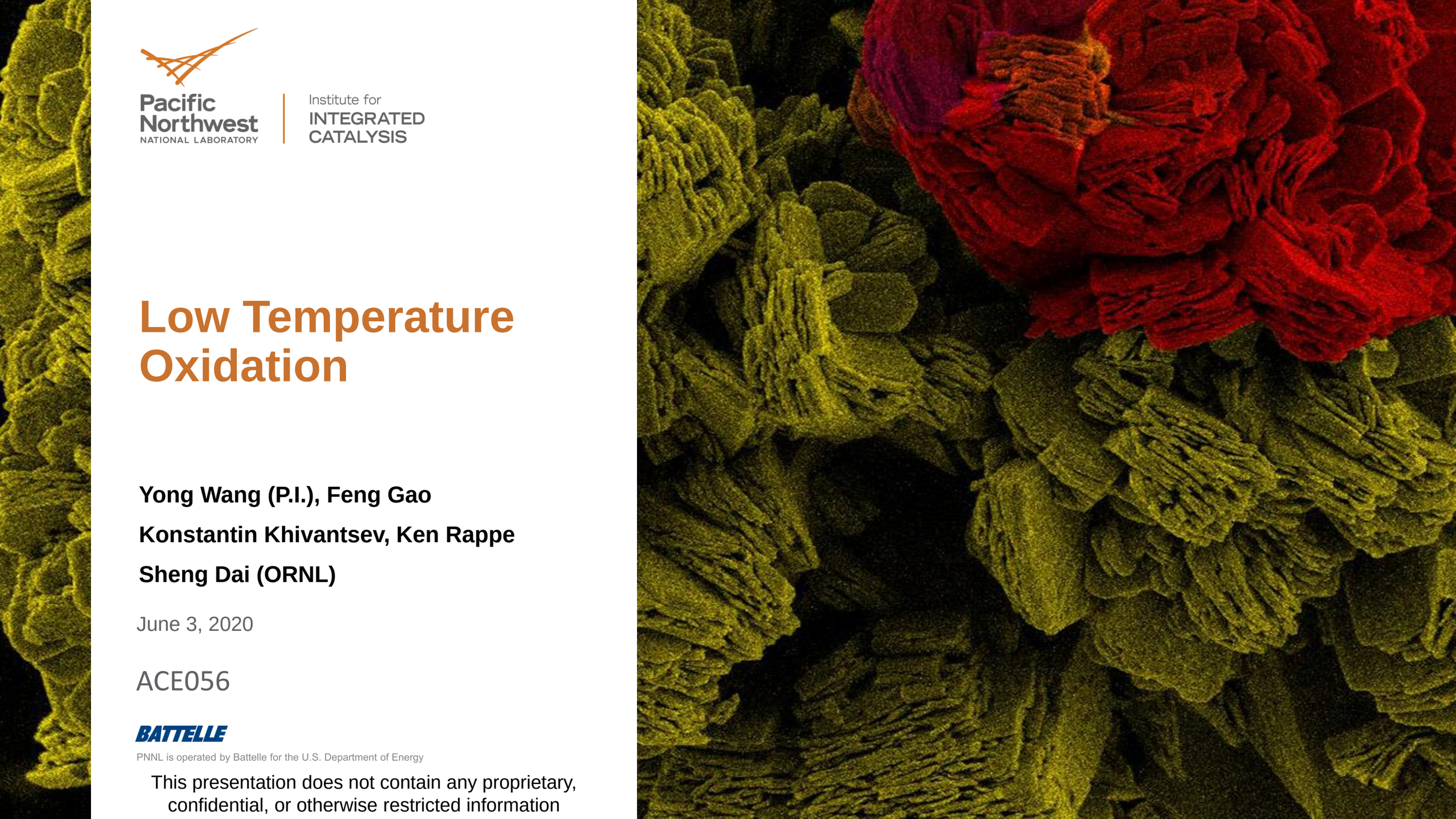

Pacific Northwest NATIONAL LABORATORY

Institute for INTEGRATED CATALYSIS

Low Temperature Oxidation

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June 3, 2020

ACE056

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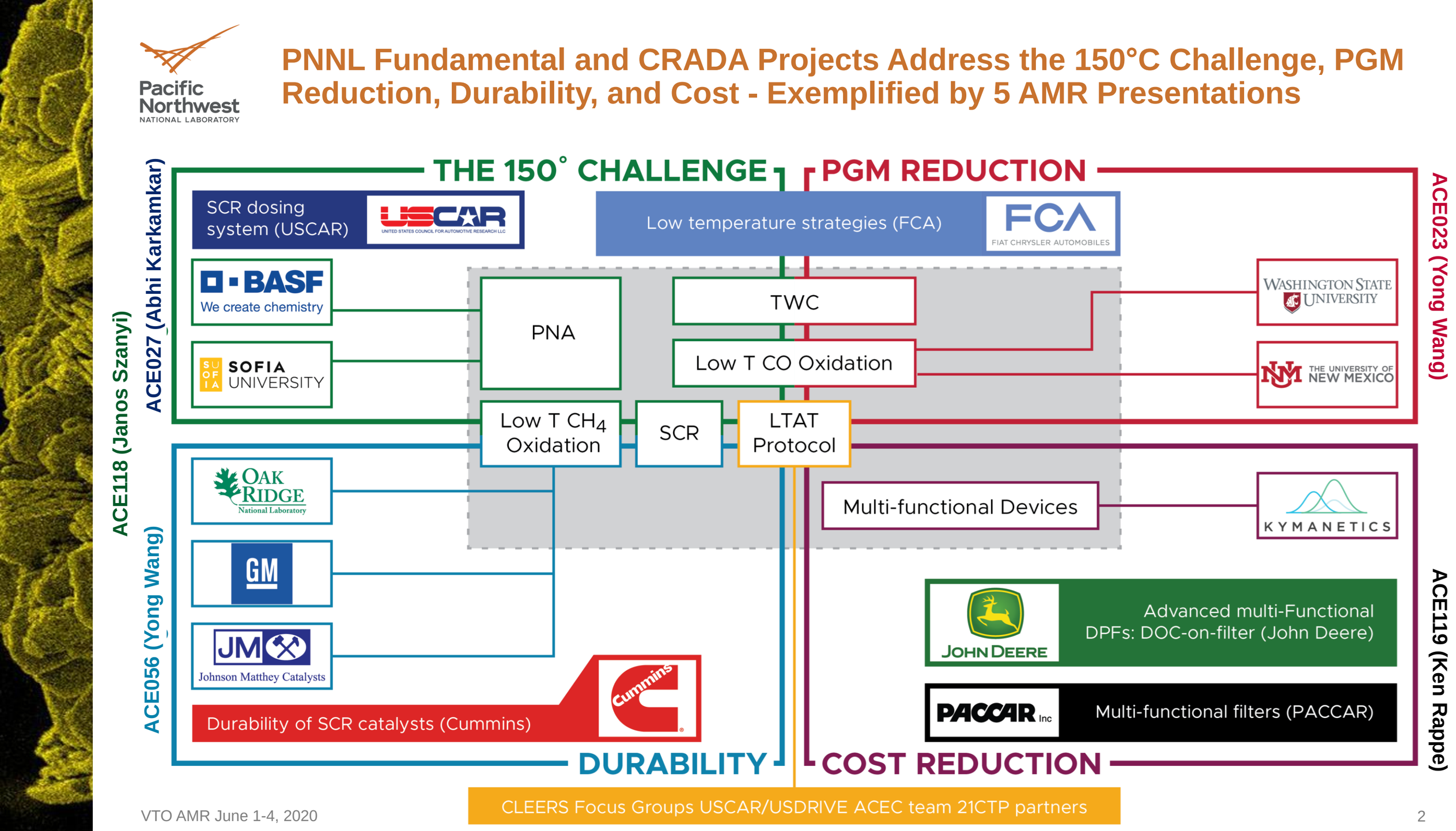
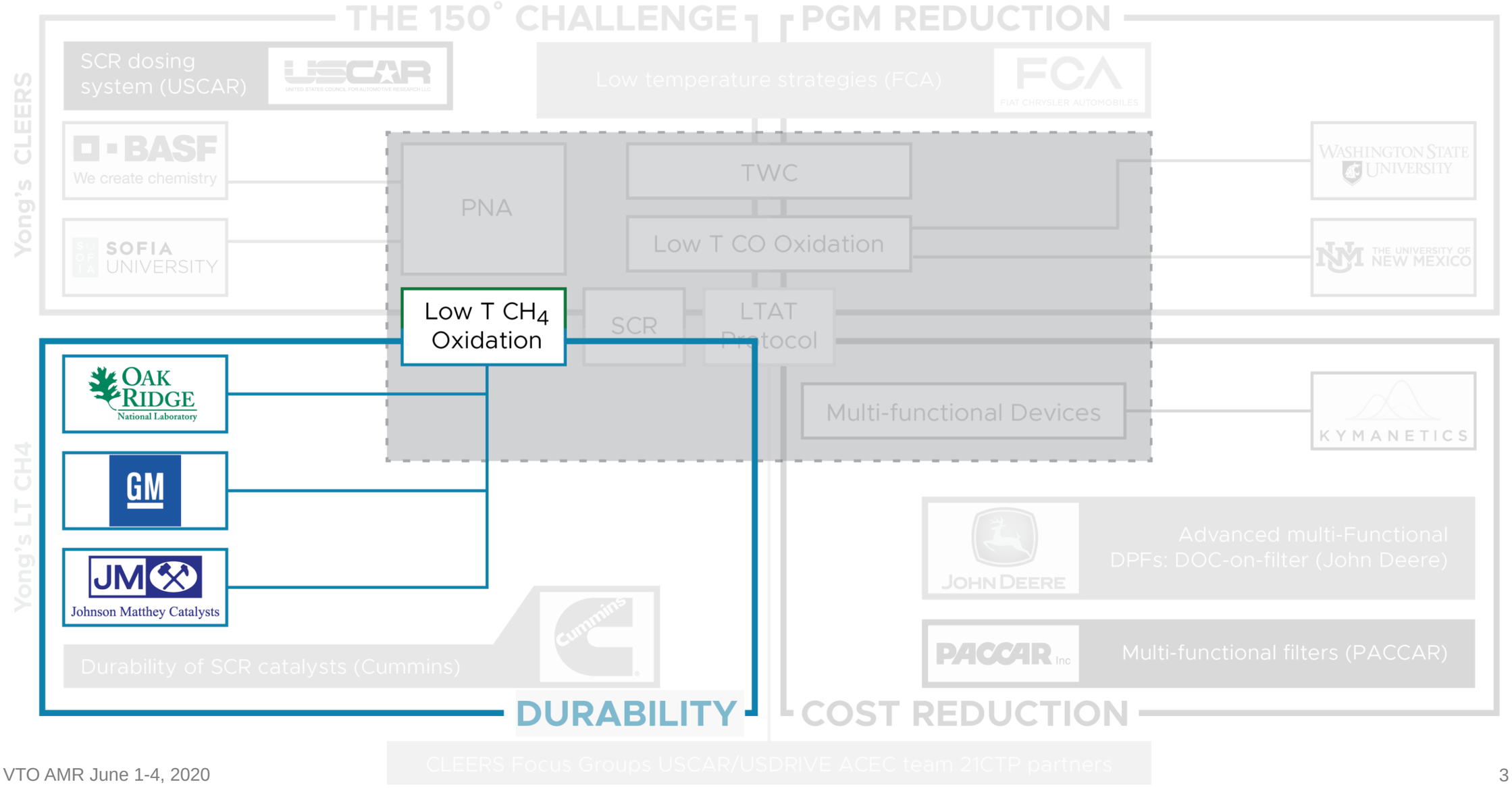
PNNL Fundamental and CRADA Projects Address the 150°C Challenge, PGM Reduction, Durability, and Cost - Exemplified by 5 AMR Presentations



Low Temperature CH_4 Oxidation Focuses on Low Temperature Activity and Catalyst Durability



Relevance

- Increasing internal combustion engine efficiency through advanced aftertreatment
  - Driven by U.S. EPA Tier 3 Bin 30 emission standard.
- Requires aftertreatment technologies integrated with the combustion approaches.
- CH_4 regulated as greenhouse gas emission
  - 100-yr global warming potential (GWP):

$$GWP_{100yr}^{CH_4} = 28 \times GWP_{100yr}^{CO_2}$$

  - Implemented on a cap basis, 30 mg/mile.
- NG engines require an aftertreatment system with improved methane (CH_4) oxidation at lower temperatures.

Overview

Timeline

- 3-yr project funded by Lab Call
- Status:
  - Start date – Dec. 2017
  - End date – Nov. 2020
- 85% complete

Budget

- FY18-FY20: $1.2M
  - PNNL - $900K
  - ORNL - $300K
- Funding received: $1.2M

Barriers

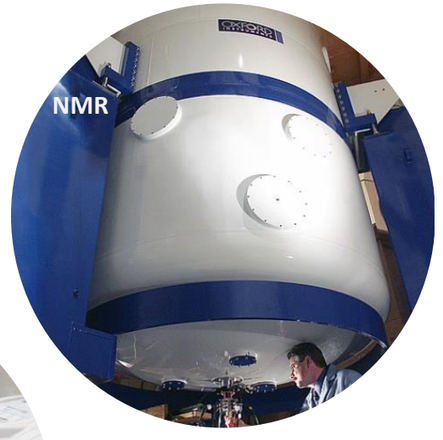
- Lack of cost-effective emission control
- Durability of emissions control devices
- Effective dissemination of information

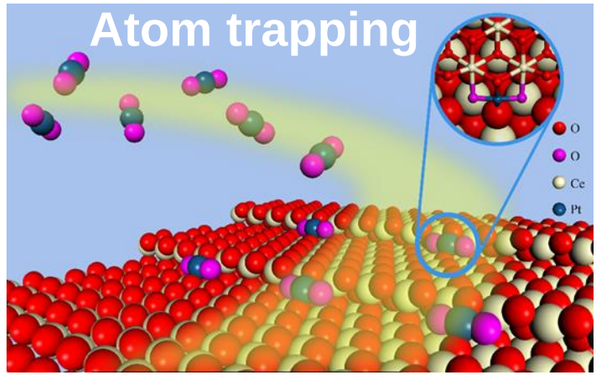
Partners

- Oak Ridge National Laboratory
- Johnson Matthey
- GM

Approach/Strategy

- Focus on Pd which shows the best performance at low temperature.
- Elucidate the nature of Pd active sites by synthesizing supported Pd catalysts with controlled nuclearity of Pd(O) and Pd-support interaction.
  - Institute for Integrated Catalysis (IIC)
  - Environmental Molecular Sciences Laboratory (EMSL)
- Increase catalyst activity by atom trapping to create thermally durable Pd single atom catalysts with reduced PGM usage.
- Demonstrate activity and durability of leading candidate catalyst formulations using U.S. DRIVE Low-Temperature Catalyst Test Protocols.



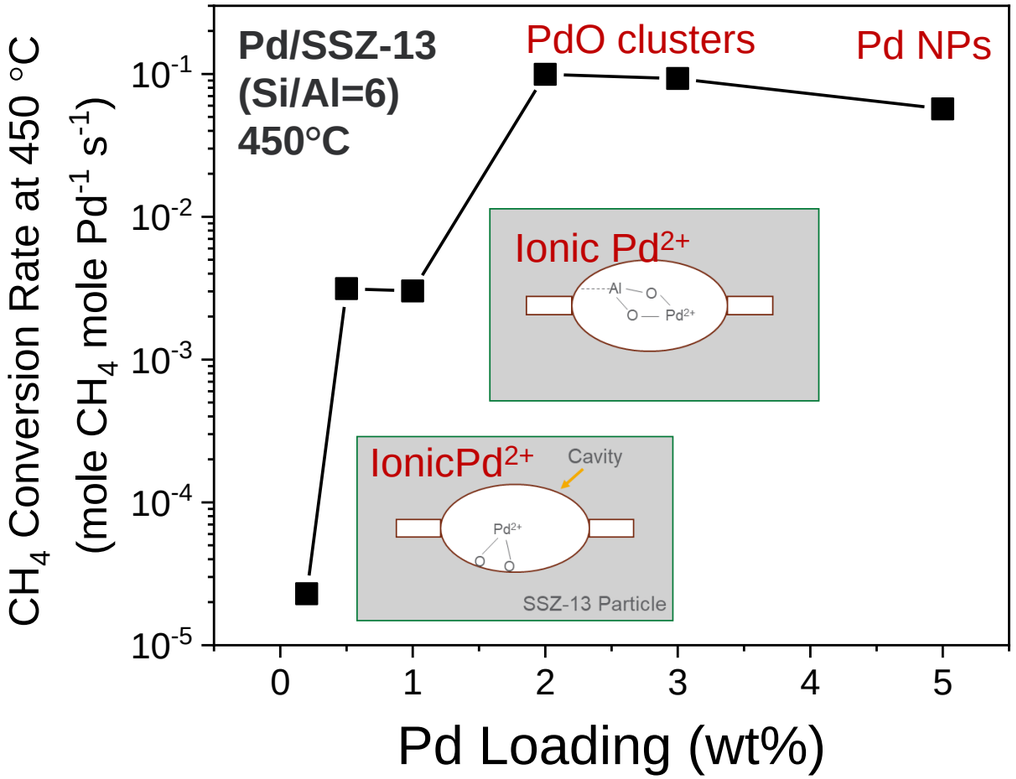


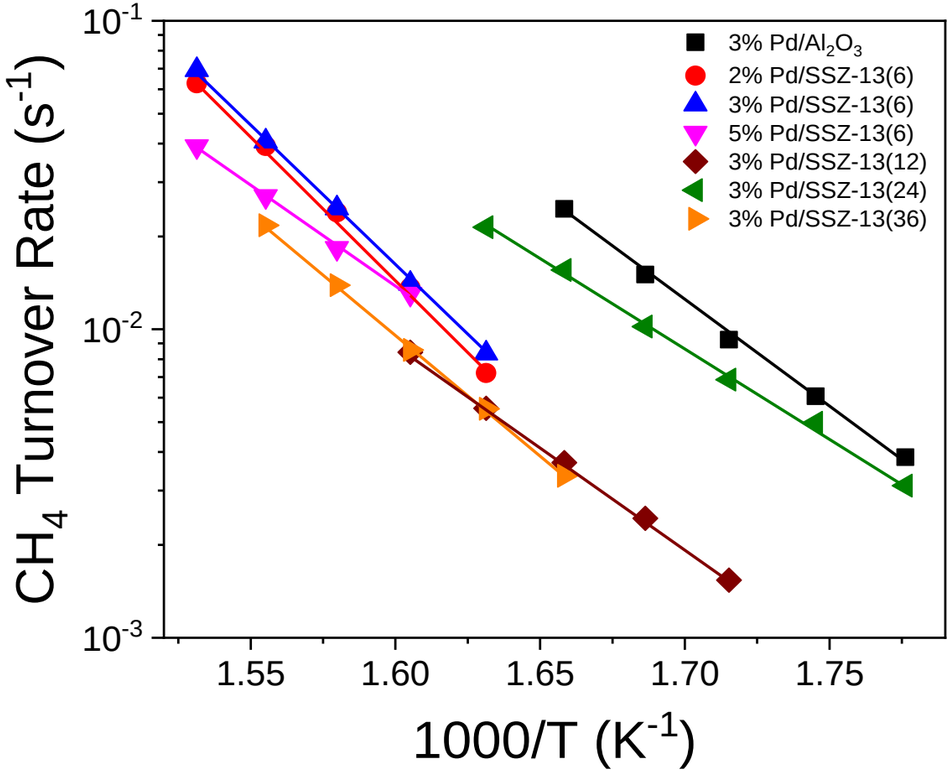
Technical Milestones

	Milestone Description	Date	Status
Go/No-Go	Demonstrate >70% methane conversion at <350°C	6/30/2019	√
Milestone	Developing bimetallic approach using single atom catalysts by atom trapping for methane combustion	11/30/2020	On track
Milestone	Demonstrate >95% methane conversion at <350°C without detrimental effect by sulfur and steam	11/30/2020	On track

Accomplishments

Confirmed that PdO Clusters/Nanoparticles Are 2-4 Orders of Magnitudes More Active Than Atomically Dispersed Ionic Pd^{2+}



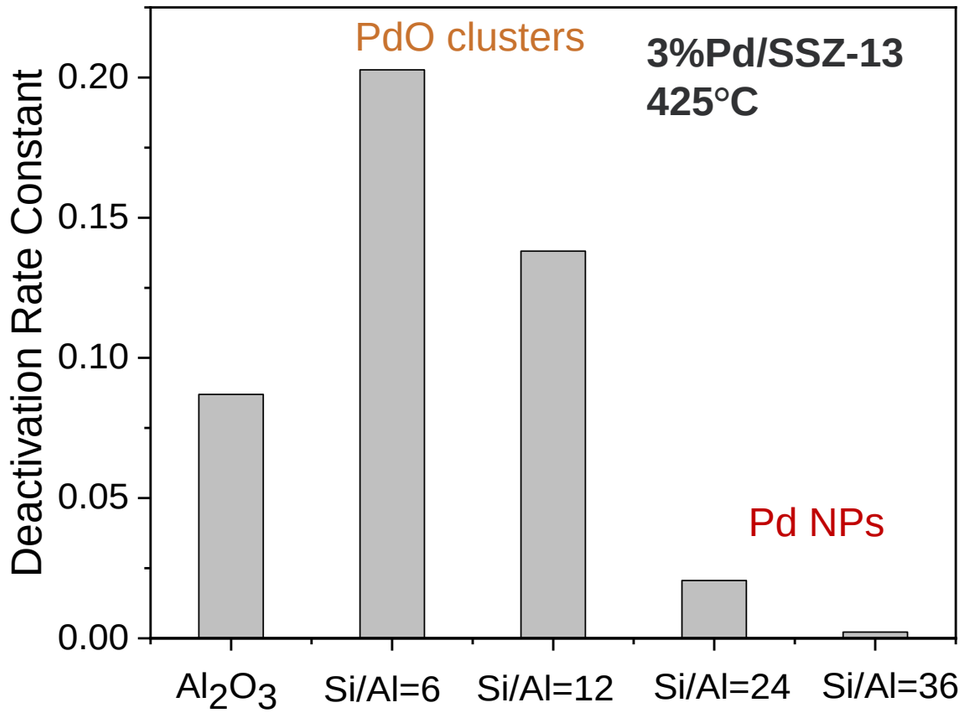


CH_4 640 ppm, 14% O_2, 5% CO_2 and ~3% H_2O, balanced with N_2

- Well-defined Pd catalysts are synthesized on SSZ-13 (Si/Al=6) as confirmed by TEM and EXAFS characterization: atomically dispersed ionic Pd^{2+}, PdO clusters (<2nm), and PdO nanoparticles (>5nms).
- Although PdO clusters/nanoparticles are much more active than atomically dispersed ionic Pd^{2+}, they exhibit similar or lower activity on SSZ-13 than on alumina, suggesting no apparent advantages with zeolite supports.

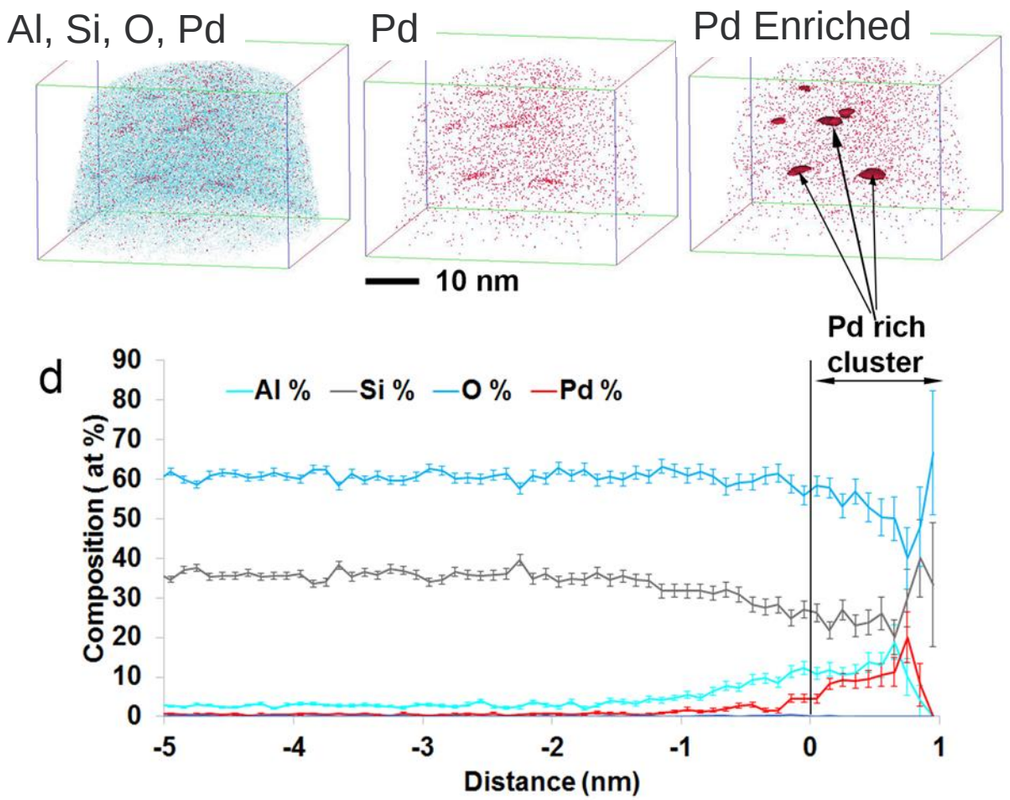
Accomplishments

PdO Clusters Deactivate due to Coverage by Al_2O_3 Formed by H_2O Induced Hydrolysis of Al^{3+}



CH_4 640 ppm, 14% O_2, 5% CO_2 and ~3% H_2O, balanced with N_2

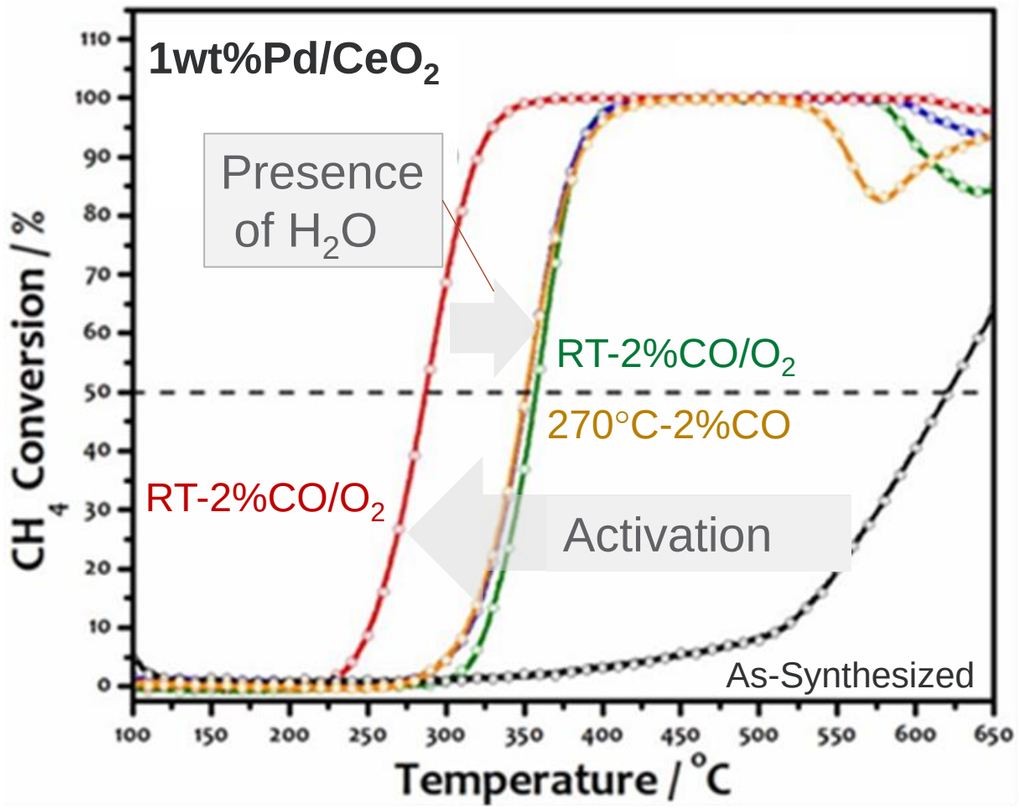
Atom Probe Tomography of Spent 2%Pd/SSZ-13(6)



- Although PdO clusters are active (like PdO nanoparticles), they deactivate more rapidly due to the formation of Al_2O_3-rich decorating layer on PdO clusters as confirmed by Atom Probe characterization.

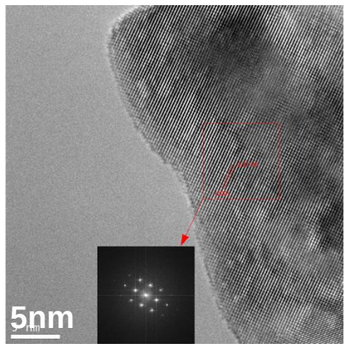
Accomplishments

CO (Ubiquitous in Auto Exhaust) Activates Pd/CeO_2 Single Atom Catalysts Prepared by Atom Trapping

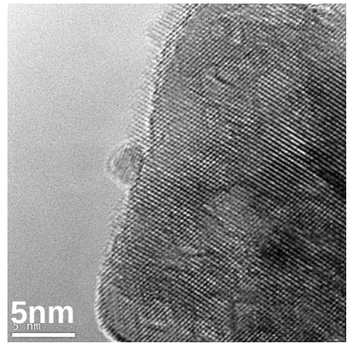


CH_4 640 ppm, 14% O_2, 5% CO_2, with or without ~3% H_2O, balanced with N_2

- As-synthesized 1wt%Pd/CeO_2 single atom catalyst by atom trapping (800°C in air) is not active due to ionic Pt^{2+}.
- Presence of CO (in feed) at room temperature activates the catalyst (T_{50} of 275°C) by forming atomically dispersed Pd clusters, as confirmed by EXAFS and TEM.
- The presence of H_2O inhibits CH_4 conversion, shifting T_{50} to 350°C.
- Reduction in CO at 270°C forms Pd nanoparticles (EXAFS, CO-IR, TEM), which exhibit similar activity as Pd nanoclusters but deactivate at 3x faster rate.



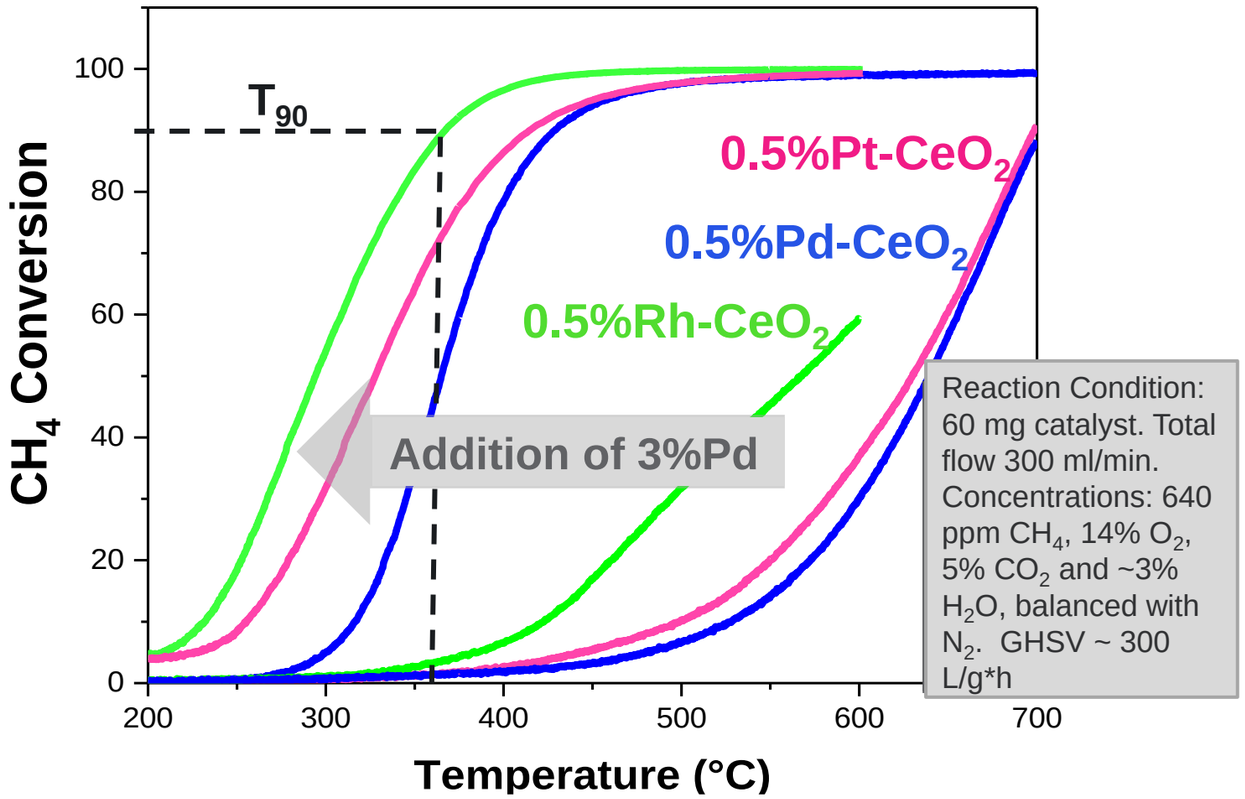
RT-2%CO/O_2



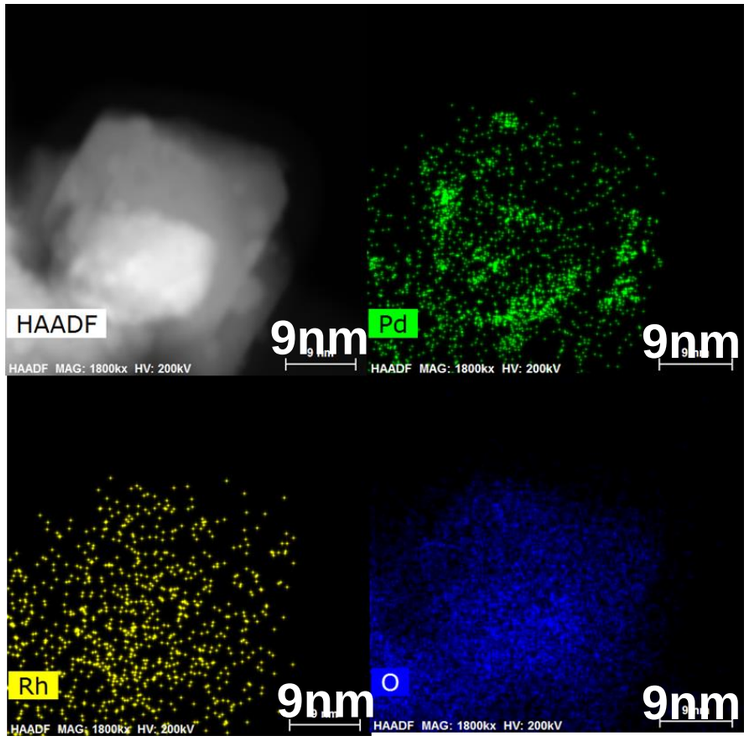
275 ºC –2%CO

Accomplishments

Adding 3% Pd to SACs Prepared by Atom Trapping Significantly Increases Activity



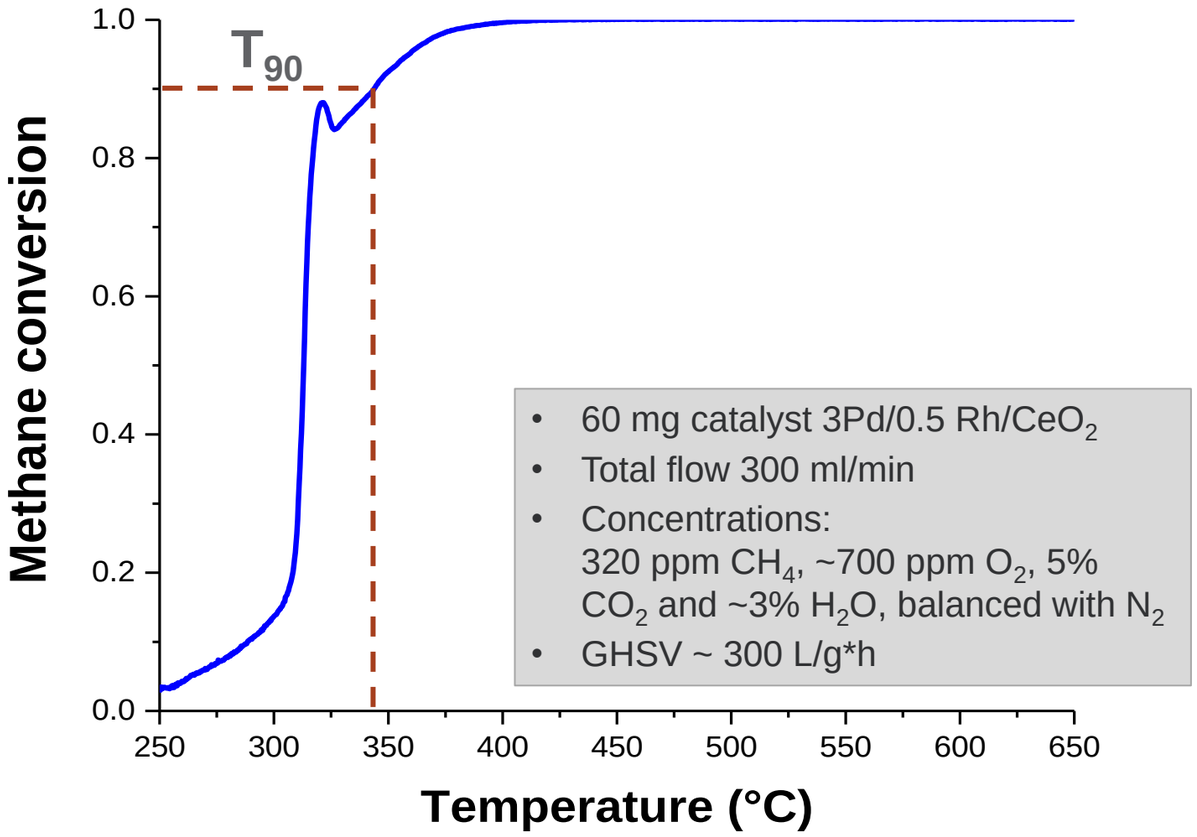
HAADF-STEM of 3%Pd on 0.5%Rh-CeO_2



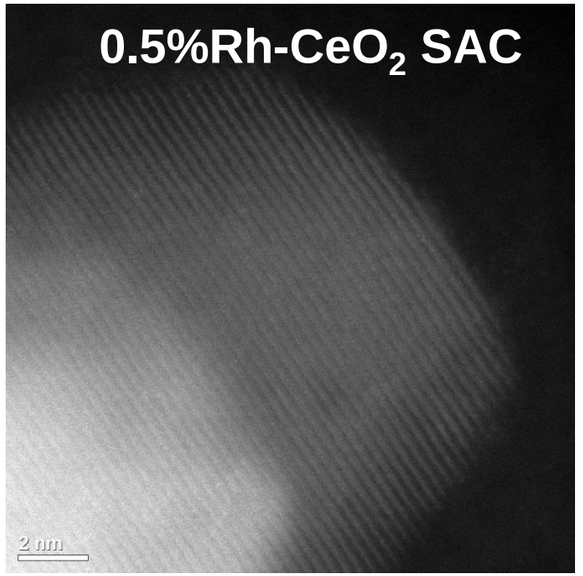
- M-O-Ce (Pt, Pd, Rh) formed by atom trapping readily activates O_2 (*Nature Comm*., 2019), and depositing PdO in proximity may provide the facile oxidation route.
- Stabilization of active PdO clusters by M-O-Ce (Pt, Pd, Rh) as confirmed HAADF-STEM.
- 3%Pd +0.5%Rh-CeO_2 reaches T_{90} of ~350°C with stable activity.

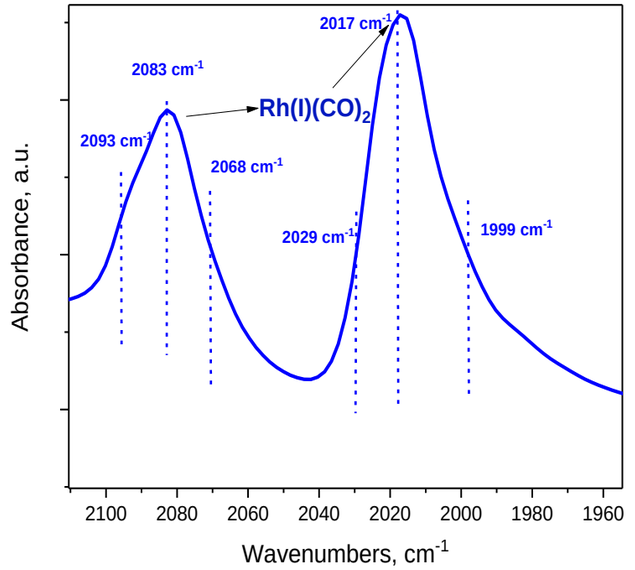
Accomplishments

Adding 3%Pd to Rh-SAC Prepared by Atom Trapping Yields Excellent Stoichiometric Activity



- 60 mg catalyst 3Pd/0.5 Rh/CeO_2
- Total flow 300 ml/min
- Concentrations: 320 ppm CH_4, ~700 ppm O_2, 5% CO_2 and ~3% H_2O, balanced with N_2
- GHSV ~ 300 L/g*h

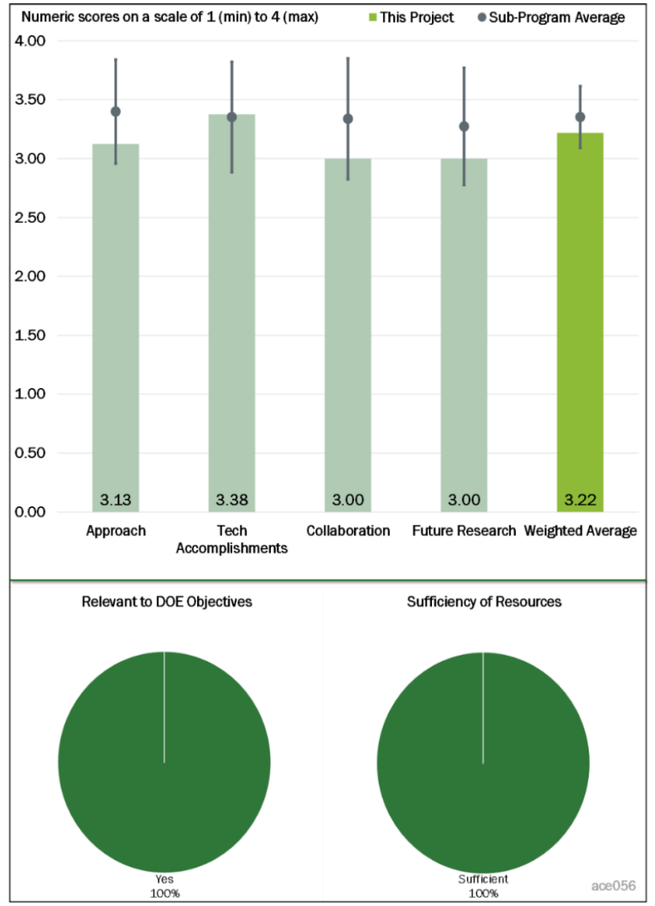




- 3%Pd +0.5%Rh-CeO_2 reaches T_{90} at <350°C
- Uniform Rh(I) confirmed by STEM and CO-IR

Responses to Previous Year Reviewers' Comments

Reviewers' Comments	PNNL Responses
Different test conditions were used.	Standardized the testing conditions among different labs with lean conditions using U.S. DRIVE Test Protocol, modifying the lean-GDI exhaust for natural gas, confirmed with ORNL.
Strengthen catalyst characterization efforts and fundamental understanding.	Focused on the understanding of the nature of Pd and roles of support interaction with EXAFS, atom probe etc. with a manuscript submitted for publication.
Worth examining the effect of feed stream stoichiometry (air-fuel ratio) on CH_4 conversion.	Expanded the studies on leading candidate formulations via consulting with GM.
Study the sulfur tolerance and also demonstrate performance on engine testing.	Sulfur tolerance was part of the planned U.S. DRIVE protocol test on leading candidate catalyst formulations which is delayed due to lab closure (COVID-19). Engine test is out of current project scope and will be proposed in future projects with partners.
Need to address the cost of Pd-based catalysts.	Reducing Pd cost is our main objective using single atom catalysts via atom trapping.



Collaboration and Coordination with Other Institutions

Acknowledgements

DOE Vehicle Technologies Program:

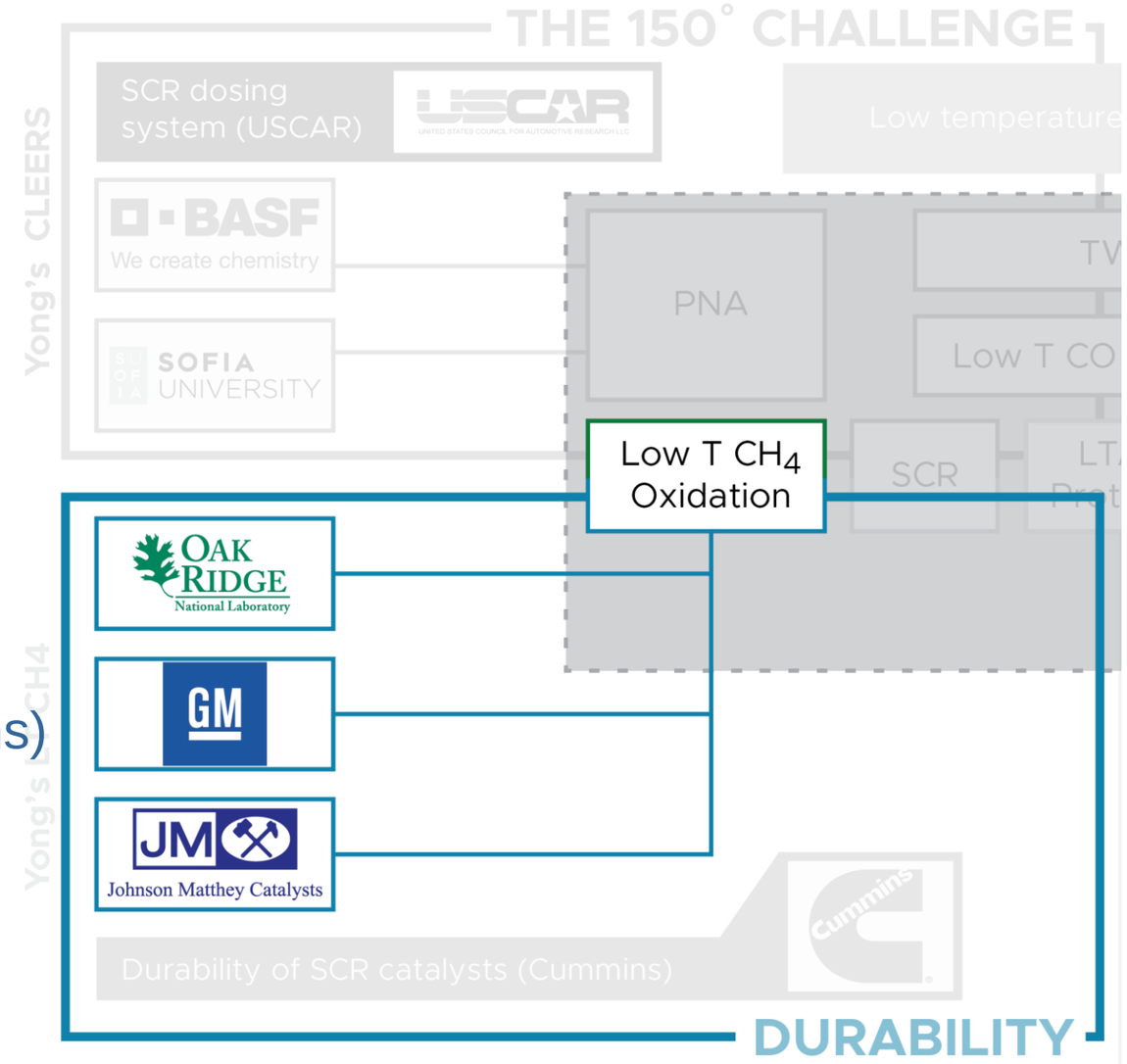
Gurpreet Singh, Ken Howden, Siddiq Khan

Sheng Dai (synthesis)
Melanie Debusk and Josh Pihl (catalyst test)

Wei Li, Se Oh
(guidance on surrogates and testing conditions)

Haiying Chen (baseline commercial samples)

Prof. Jeff Miller, Purdue University (EXAFS)



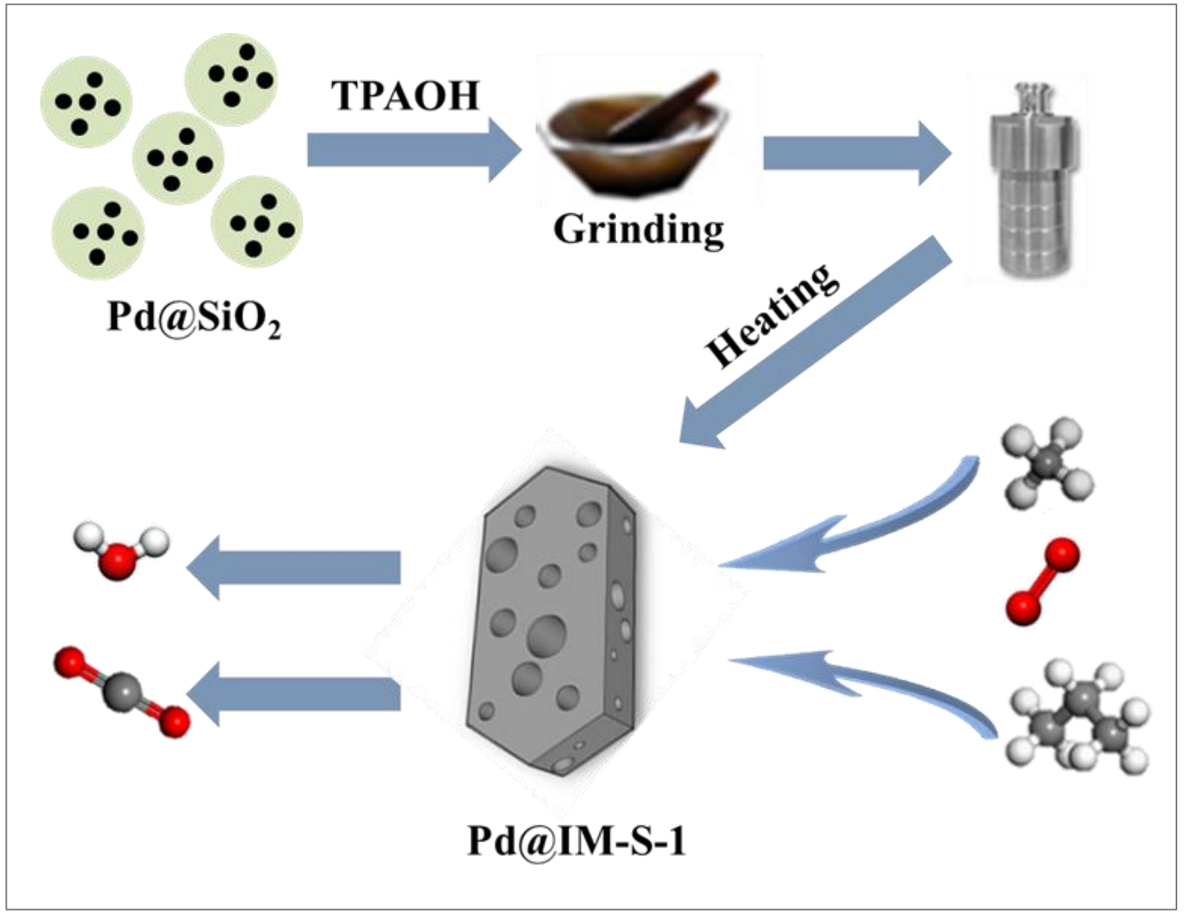
Remaining Challenges and Barriers

- Reduce water inhibition on catalyst activity at low temperatures
- Improve catalyst cyclic stability
- Thrift the precious metal usage to further reduce catalyst cost
- Mitigate catalyst deactivation, e.g, by sulfur poison

Proposed Future Work

- Durability studies of leading candidate catalyst formulations, e.g., Pd-Rh single atom catalysts prepared by atom trapping, including sulfur tolerance using U.S. DRIVE protocols
- Synthesis of supported Pd which is tolerance to water, has minimal interaction with support while being sintering resistant, e.g. embedded Pd in hydrophobic zeolites

Silicate-1-confined Pd via *in situ* mesoporogen-free synthesis



Summary

- Kinetic studies and advanced characterization provide guidance on the design of active and durable Pd catalysts for CH_4 oxidation: facile activation/delivery of oxygen and stabilization of PdO while minimizing Al^{3+} interactions.
  - Isolated Pd^{2+} sites are 2-4 orders of magnitude less active than PdO clusters/particles, mainly due to the low activity of lattice oxygen that pairs with the Pd^{2+} ions.
  - PdO clusters and nanoparticles show similar activity.
  - Stabilization of PdO clusters by support containing Al^{3+} forms Al_2O_3-rich layer on PdO clusters, leading to catalyst deactivation via same deactivation mechanism as commercial Pd/Al_2O_3 catalysts.
- Bimetallic Pd-Rh and Pd-Pt catalysts prepared via atom trapping to create single atoms exhibit superb activities, e.g., achieving 90% CH_4 conversion at 350°C.

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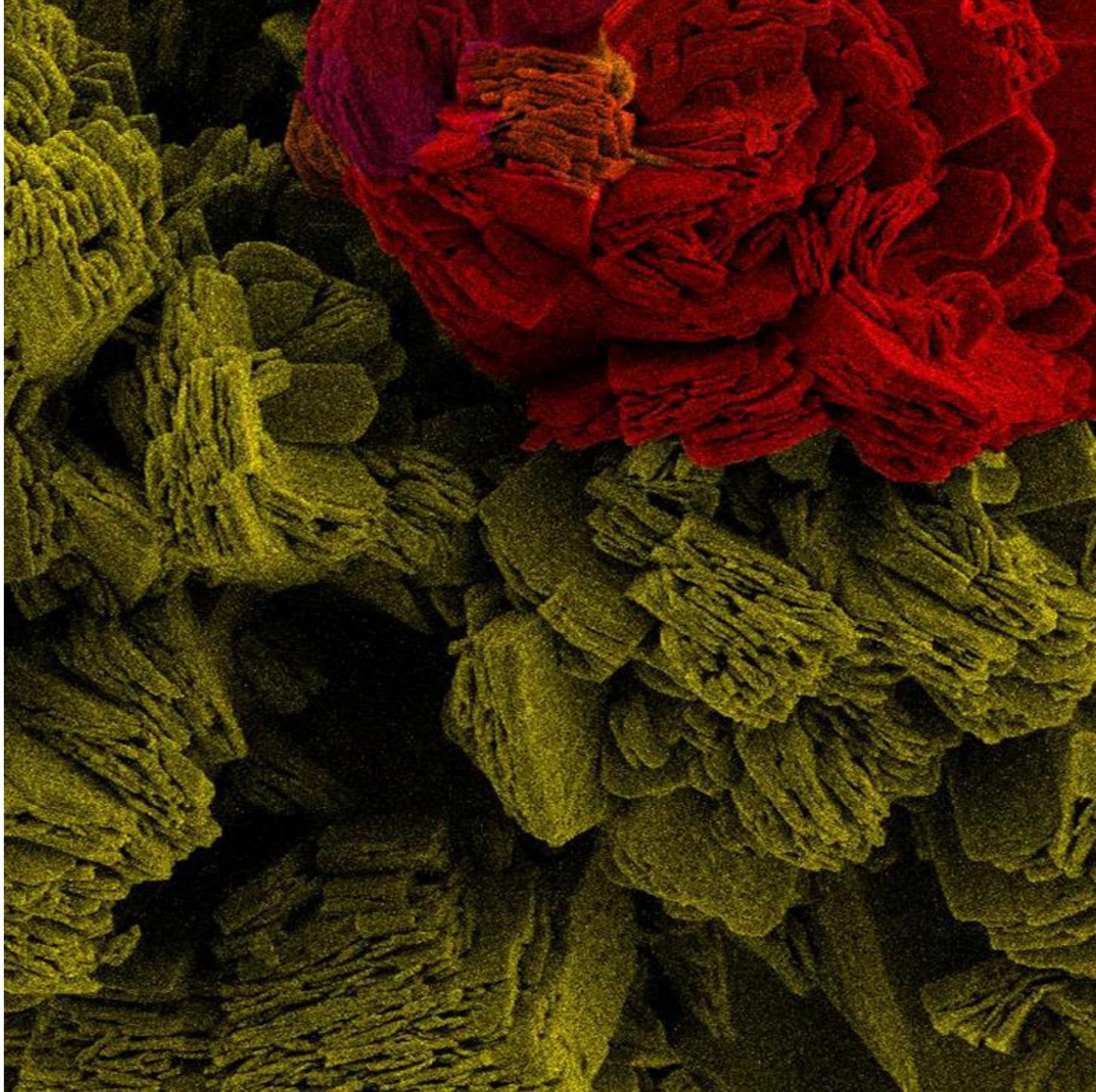
Thank you



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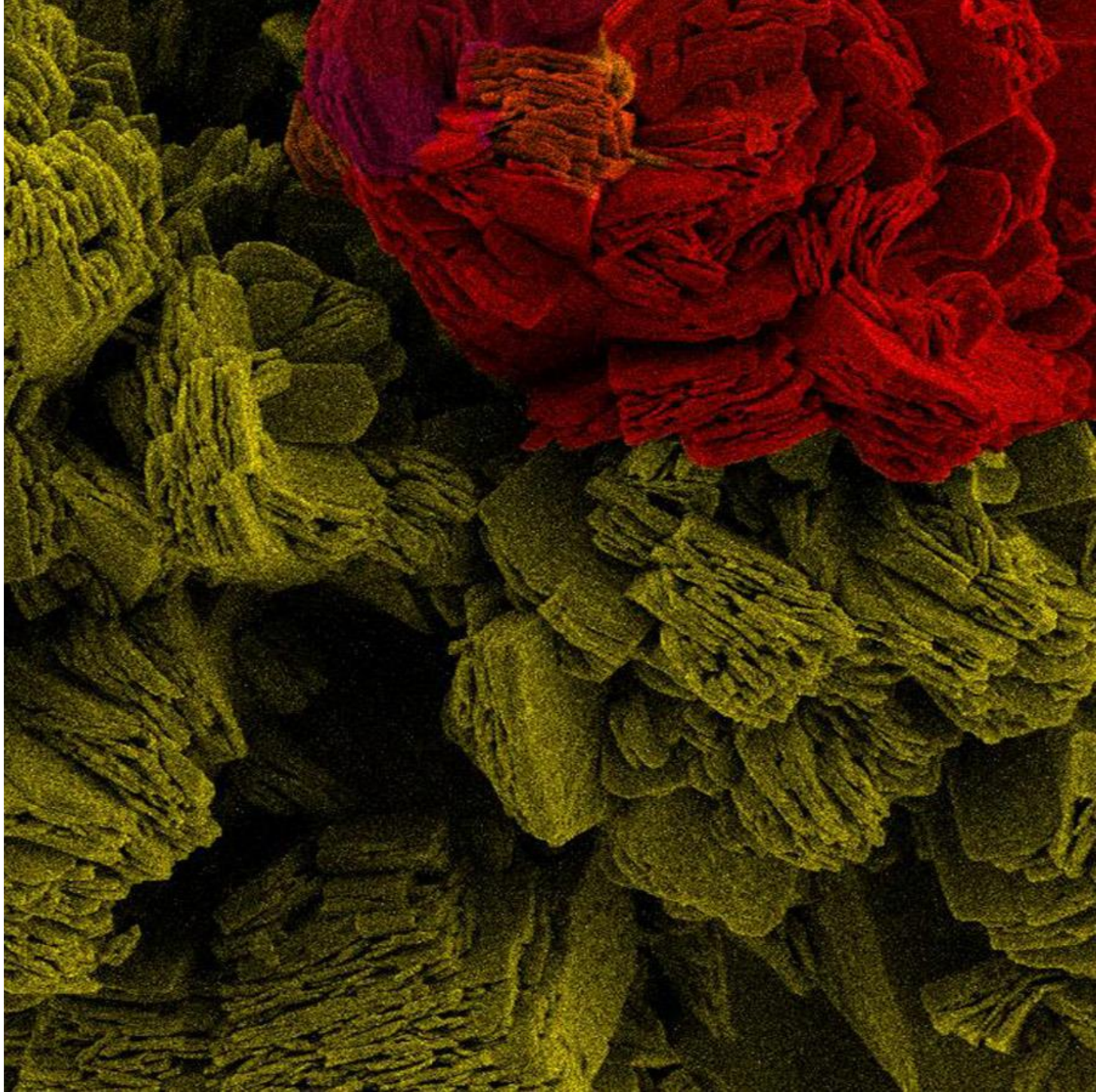
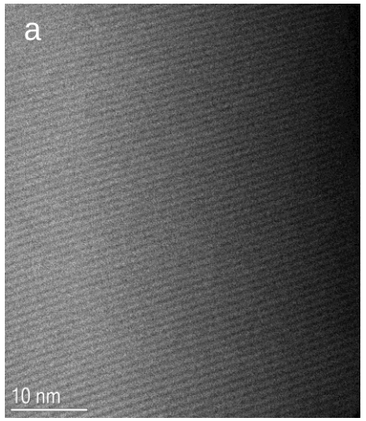
Technical Backup Slides

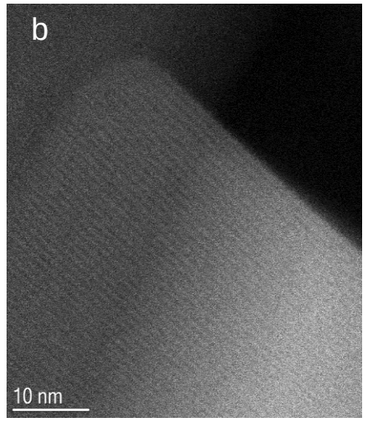


VTO AMR June 1-4, 2020

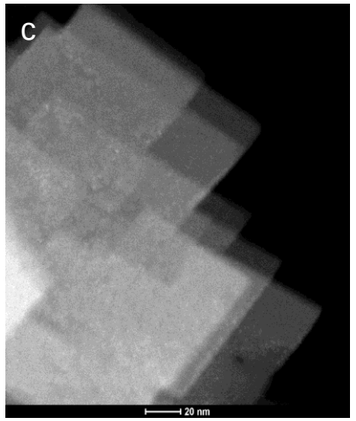
TEM Characterization of Pd/SSZ-13 Catalysts (before imaging, all catalysts were stabilized under wet (~3% H_2O) methane combustion conditions for ~20 h at ~400 °C)



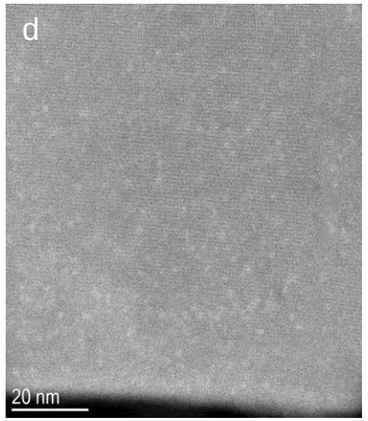
0.2% Pd/SSZ-13(6)



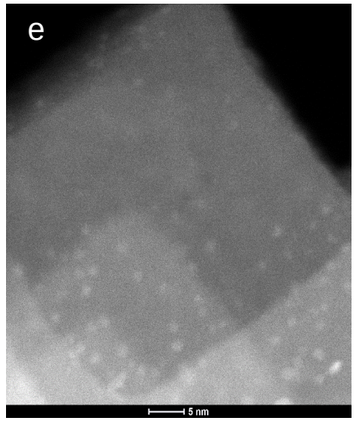
1% Pd/SSZ-13(6)



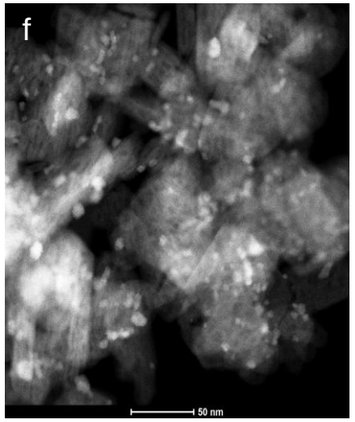
2% Pd/SSZ-13(6)



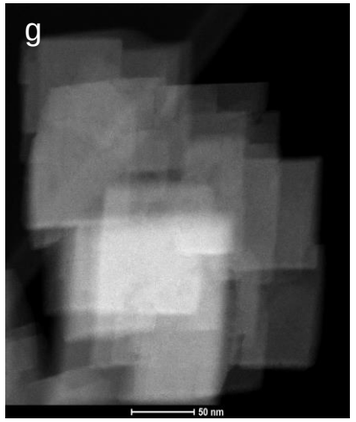
3% Pd/SSZ-13(6)



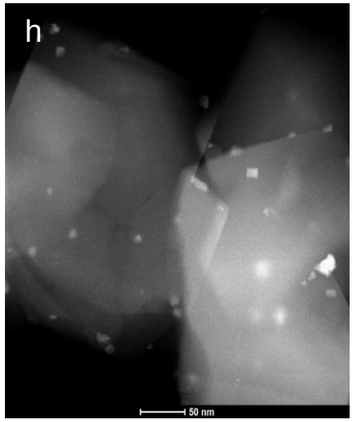
5% Pd/SSZ-13(6)



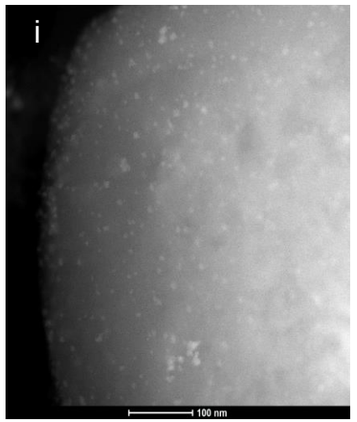
3% Pd/Al_2O_3



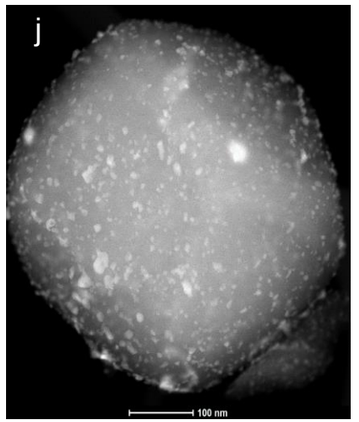
3% Pd/SSZ-13(6)



3% Pd/SSZ-13(12)

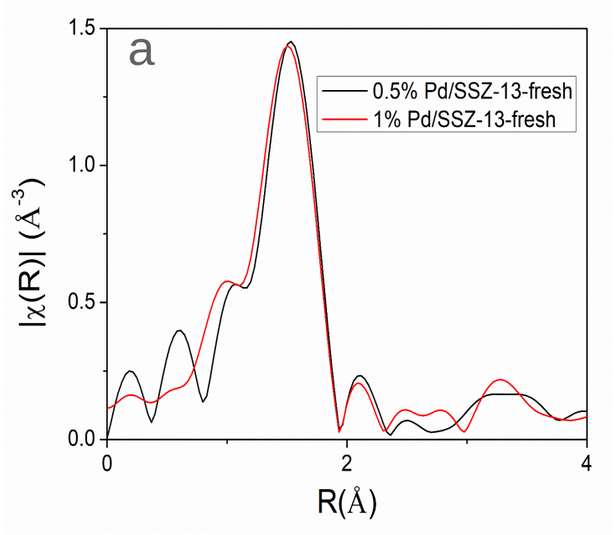


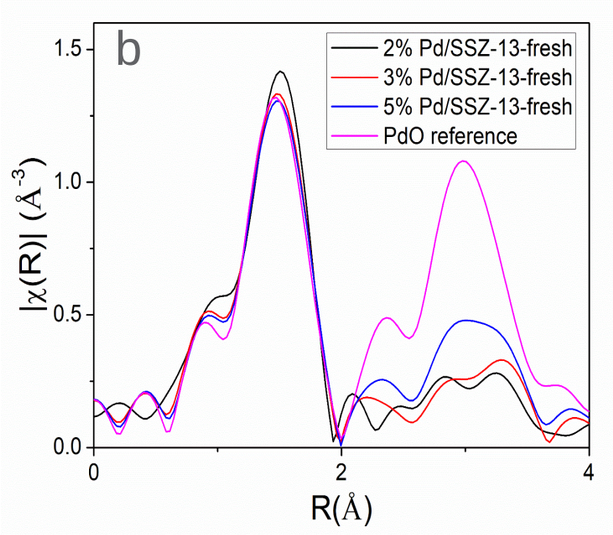
3% Pd/SSZ-13(24)

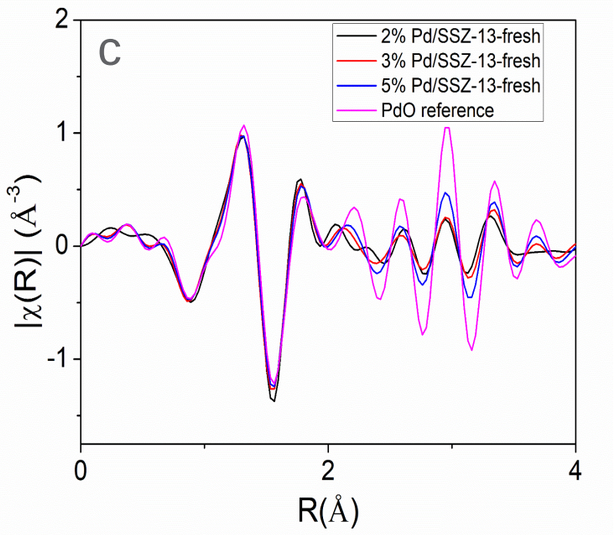


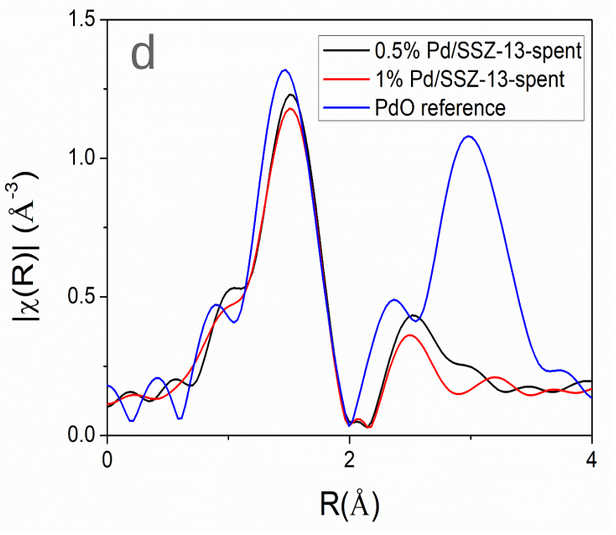
3% Pd/SSZ-13(36)

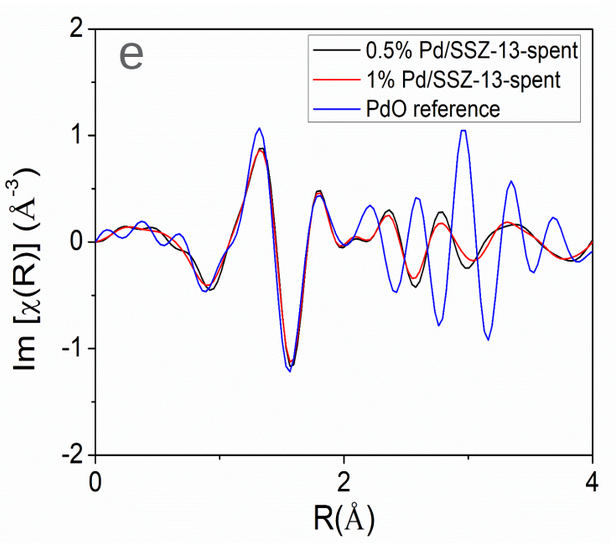
Pd K Edge Extended X-ray Absorption Fine Structure (EXAFS) Spectra for Fresh and Used Pd/SSZ-13(6) Catalysts

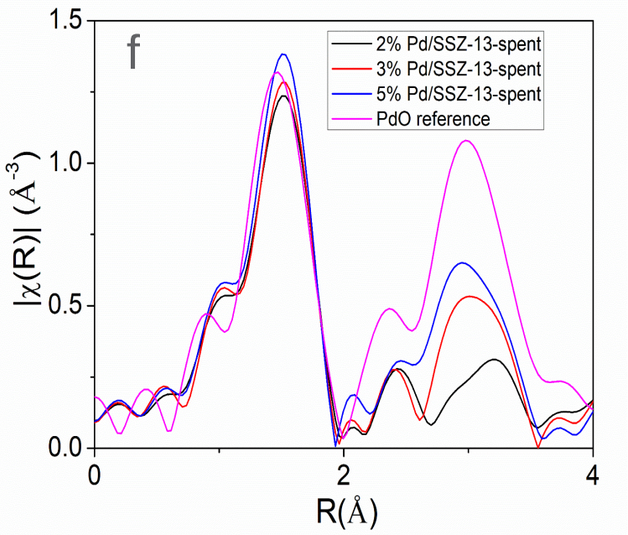




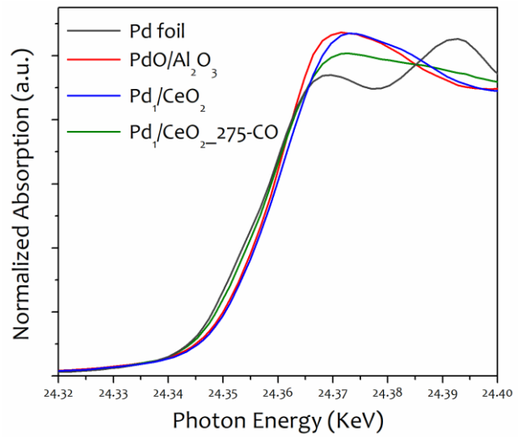


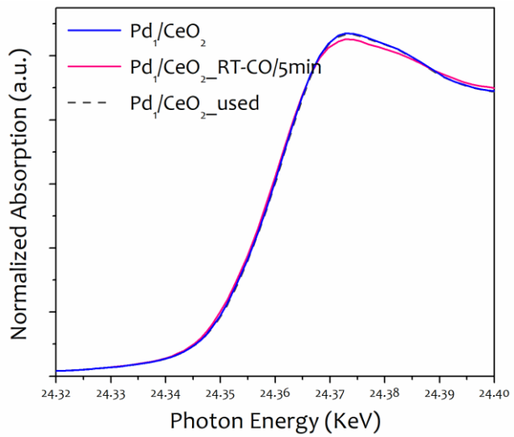


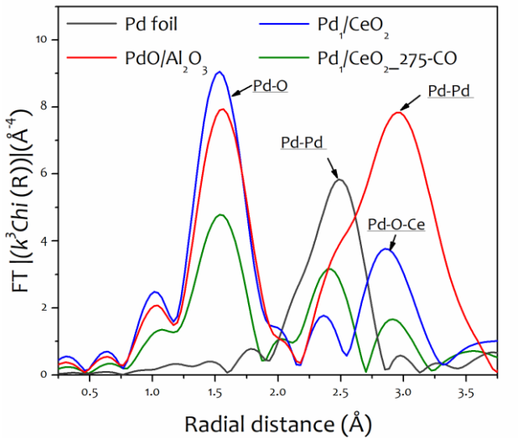


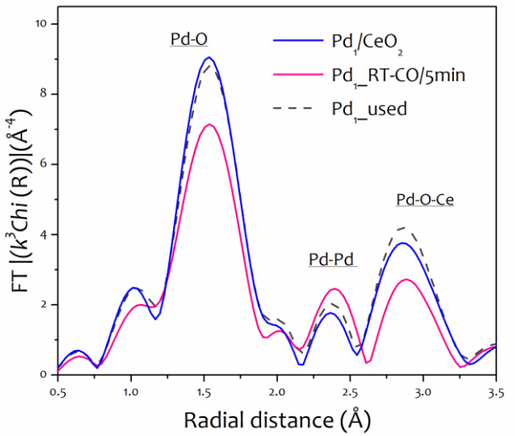


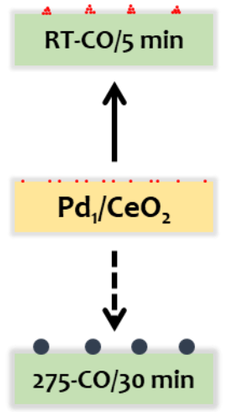
X-Ray Absorption Characterization of Pd/CeO_2 Catalysts and Catalyst Deactivation Rate Measurements

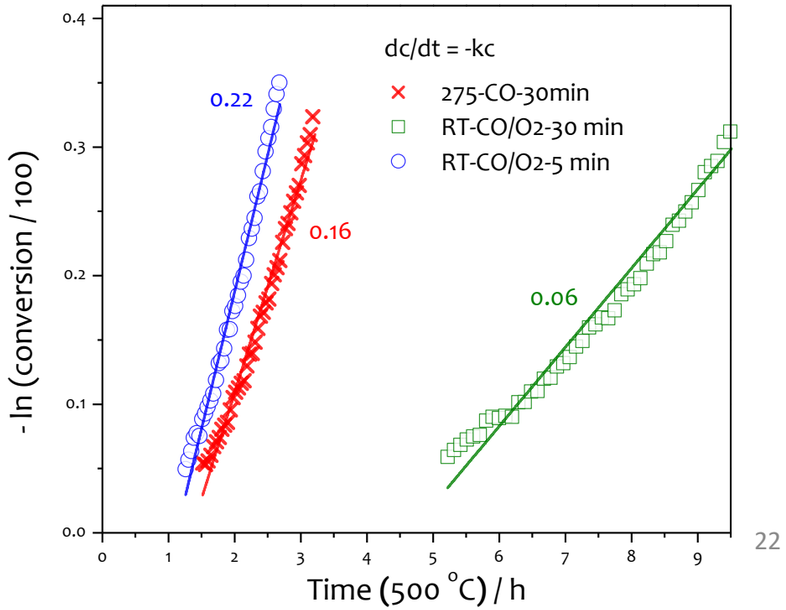












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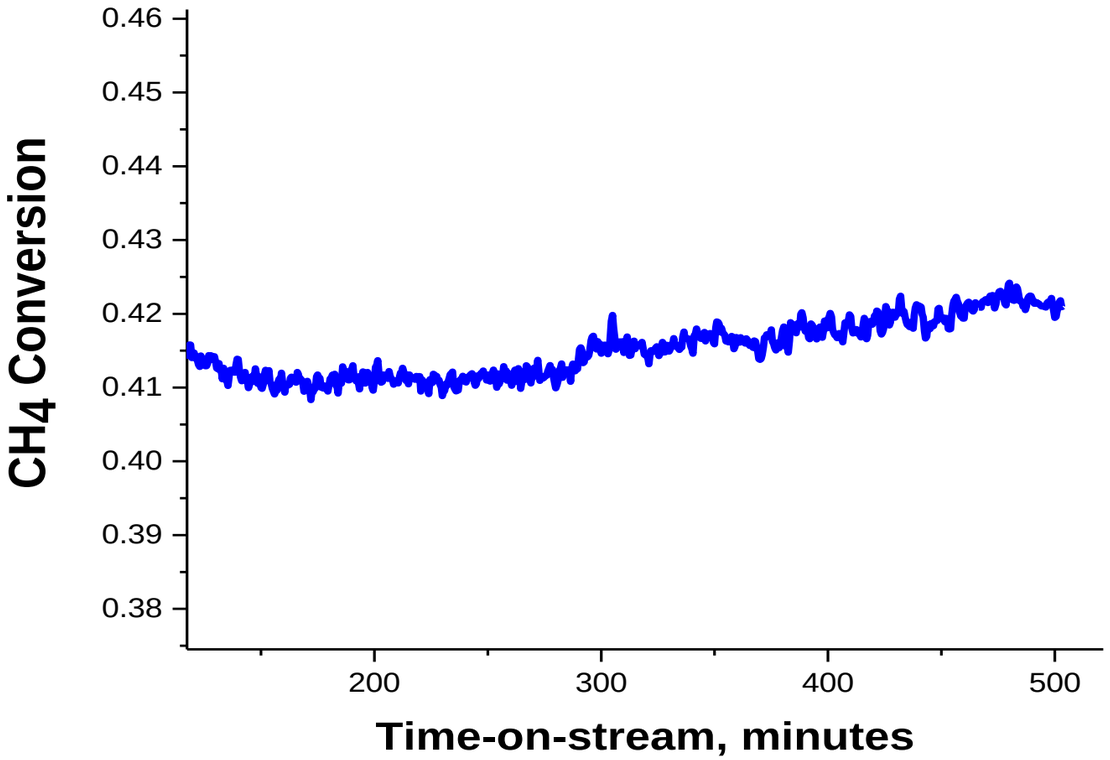
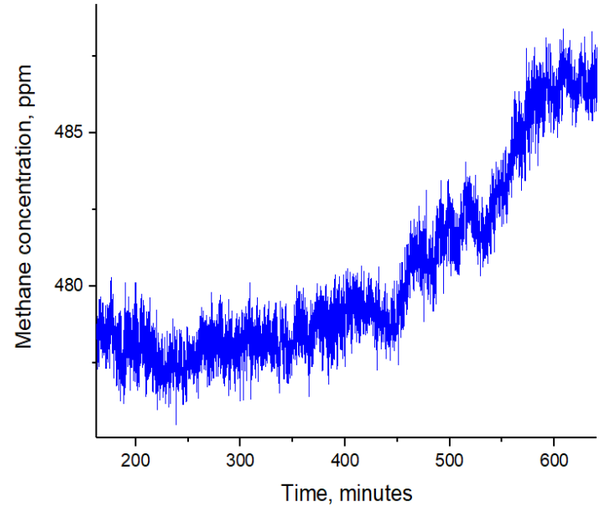
Catalyst Stability Measurements

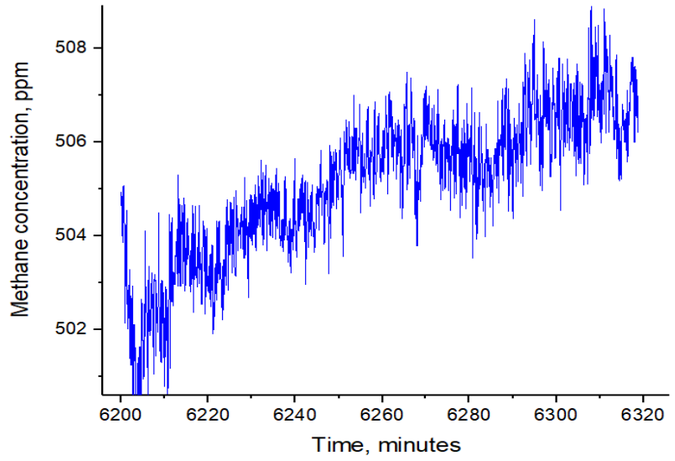
Stability of 3wt%Pd on 1wt% Pt/Ceria at 360°C



Reaction Condition: 60 mg catalyst 3 wt% Pd/1wt%Pt/CeO2.at 360 °C. Total flow 300 ml/min.
Concentrations: 640 ppm CH_4, 14% O_2, 5% CO_2 and ~3% H_2O, balanced with N_2. GHSV ~ 300 L/g*h

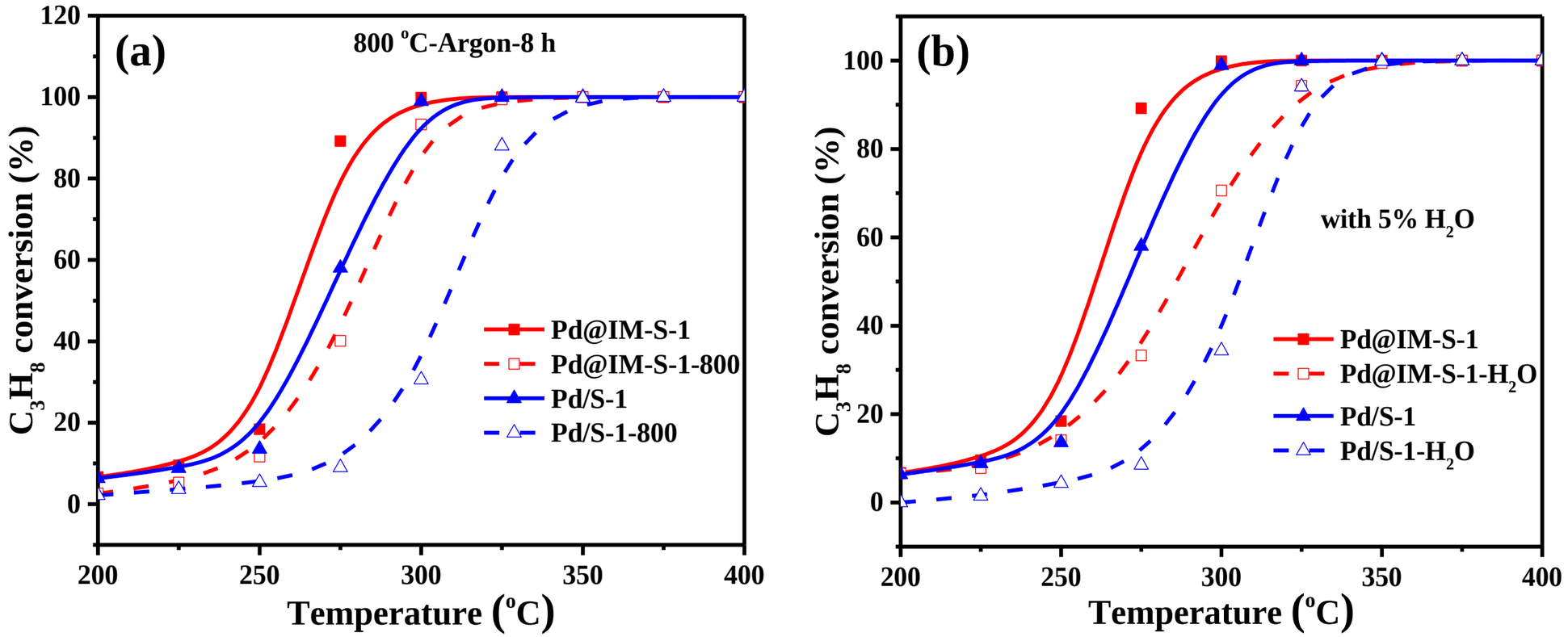
Stability of the 3 wt%Pd/SSZ-39 (800 °C HTA) 425 °C





- Catalyst is stable
- (<5% decrease within 105 hrs)

Thermal Stability Test (a) and Water Resistance Test (b) of Pd@IM-S-1 and Pd/S-1 in the Oxidation of Propane



Conditions: 2000 ppm C_3H_8, 10% O_2 , balanced with N_2 , and the WHSV was 36 000 mL $g_{cat.}^{-1}$ h^{-1}